calculation for each term and their sum which contribute to ΔG are reported in Table II. In any case, the entropy of the reactions is unfavorable and particularly for photoreduction in CO.

The enthalpy, ΔH, is calculated in Table III from the energy balance of the bonds created and destroyed in reactions 13-16. The Ni-O and Ni-CO bond energies are taken as 24 and 30 kcal mol^{-1} from theoretical calculation where Ni is in a zerovalent state.[47] These values are not known for Ni^{2+} and Ni^{+} ions, but one can expect that the difference of the bond energies does not change drastically with the oxidation state of nickel. The $Ni^{+}-H_2$ bond energy is evaluated to be 8.5 kcal mol^{-1},[32] and the O-H and O-C bond energies are taken from the literature.[55] In conclusion, whatever the pressure (reactions 13-15) and the nature (reactions 15 and 16) of the gas, the photoreduction is thermodynamically highly favorable since ΔG ranges from -116.5 to -146 kcal mol^{-1}.

Registry No. Ni^{2+}, 14701-22-5; SiO_2, 7631-86-9; Ni^{+}, 14903-34-5; H_2, 1333-74-0; CO, 630-08-0; Ni, 7440-02-0.

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Mechanism of the Reaction of Nitric Oxide, Ammonia, and Oxygen over Vanadia Catalysts. 1. The Role of Oxygen Studied by Way of Isotopic Transients under Dilute Conditions

Frans J. J. G. Janssen,* Frans M. G. van den Kerkhof,

Department of Chemical Research, Research and Development Division, Arnhem Institutions of the Dutch Electricity Utilities, NV KEMA, 6800 ET Arnhem, The Netherlands

Hans Bosch, and Julian R. H. Ross

Department of Chemical Technology, Twente University of Technology, 7500 AE Enschede, The Netherlands

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The mechanism of the selective reduction of nitric oxide with ammonia in the presence of labeled oxygen has been investigated over a series of catalysts consisting of unsupported V_2O_5, V_2O_5 on TiO_2, V_2O_5 on SiO_2/Al_2O_3, and V_2O_5 on Al_2O_3. The results confirm that lattice oxygen participates in the reaction. It is shown that this participation can be explained in terms of a reduction/oxidation mechanism. Water, produced as a result of the reaction involving NO, NH_3, and O_2, is formed at two sites; the first part comes from the reaction of gaseous nitric oxide and adsorbed ammonia via an Eley-Rideal mechanism and the other comes from a surface dehydration process. The experimental findings are explained by a slightly modified and extended version of a mechanism proposed earlier.

Introduction

There is an increasing demand in Western Europe for a reduction in the level of NO_x emissions (x = 1, 2) coming from man-made sources. Such emissions are blamed for the production of "acid rain" and for other environmental problems. Selective catalytic reduction is one of the possible options for postcombustion control of emissions from stationary sources (i.e., power stations).[1a] Ammonia has been found to be a selective reducing agent for NO_x. Selective reduction is necessary because of the presence in most flue gases of oxygen (1-5%), which would react with unselective reducing agents such as carbon monoxide and alkanes. It has been shown that the selective reduction of NO_x by ammonia occurs more rapidly in the presence of oxygen than in its absence and that oxygen participates in the reaction;[1-4] it has been found that the influence of oxygen during reduction experiments is considerable even when its concentration is below 1% in volume.

Most of the mechanistic work done on the system NO/NH_3 has excluded the presence of oxygen; therefore, very little is known as yet about the behavior of oxygen during the reduction of NO with NH_3.[5-12] In addition, the exchangeability of oxygen with supported catalysts has received little attention. The only article of which we are aware describes the effect of labeled oxygen ($^{18}O_2$ throughout) on the reduction of NO over copper vanadate; these experiments were carried out in a low-pressure gas-circulation reactor system.[13]

In a previous paper[14] we described experiments in which monolayer and commercial catalysts were compared using two types of experimental systems, that of the continuous flow type and that of the pulse type. It was found that at least two types of active site were present on the surface of the catalyst and that

TABLE I: Catalysts Used in This Study

no.	catalyst	content, V wt %	S_{BET}, $m^2 \cdot g^{-1}$	particle size, mm	surface V=O, mmol·(g·catalyst)$^{-1}$
1	V_2O_5/TiO_2[a]	1.9	45	0.3-0.6	0.31
2	$V_2O_5/SiO_2/Al_2O_3$	5.6	140	0.25-0.5	0.40
3	V_2O_5/Al_2O_3	8	170	0.25-0.5	0.48
4	V_2O_5/Al_2O_3	4.4	207	0.25-0.5	0.59
5	V_2O_5	58	10.5	0.25-0.5	0.043

[a] Monolayer.

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these sites are probably due to the presence of vanadium species with valences of both +4 and +5. Two different reactions occur on these different sites: the oxidized sites can be reduced by ammonia while reoxidation can be brought about by ambient oxygen, by lattice oxygen from underlying layers, or by the oxygen of NO, depending on the reaction conditions. The main objective of this study was to study the role of O_2 in the reduction of NO by NH_3. Attention was given to the formation of N_2O and the interaction of NO with the surface during the reaction. This paper describes an investigation of the mechanism of the reduction of NO with NH_3 over the catalyst series consisting of unsupported V_2O_5, V_2O_5 on TiO_2, V_2O_5 on SiO_3/Al_2O_3, and V_2O_5 on Al_2O_5 in the presence of $^{18}O_2$ or $^{16}O_2$ at concentration levels of about 500 ppm for NO and NH_3. The role of oxygen is discussed in both a qualitative and a quantitative sense.

Experimental Section

Preparation of the Catalysts. The catalysts used in this study and their main characteristics are summarized in Table I. The V_2O_5 on TiO_2 monolayer catalyst (**1**) was prepared as described previously[15,16] by adsorption of vanadyl acetylacetonate from solution in toluene on a sample of TiO_2 consisting of anatase (68% w/w) and rutile (32% w/w). A sample of commercially available material (Ventron, West Germany) containing V_2O_5 on SiO_2/Al_2O_3 (**2**) was also examined. The catalyst V_2O_5 on Al_2O_5 (**3**) was made by wet impregnation of Al_2O_3 with an acidified solution (pH 4) of ammonium metavanadate followed by calcination in a stream of air at 450 °C. Two of the catalysts, V_2O_5 on Al_2O_3 (**4**) and unsupported V_2O_5 (**5**), were obtained from Utrecht University (The Netherlands). The powdered catalysts were pelleted, crushed, and sieved into the fraction given in Table I. Prior to the NO reduction experiments, the catalyst samples were calcined at 300–400 °C in situ in a flow of helium containing 25% oxygen.

Characterization of the Catalysts. The vanadium contents of the catalysts were determined by using X-ray fluorescence (Philips PW 1410/20). The BET surface areas were obtained by using a Carlo Erba Sorptomatic (Type 1800) system controlled by an Apple computer system. Table I also gives the concentration of V=O groups on the surface of each of the catalysts. This was determined according to the rectangular pulse technique,[17] modified as described in ref 14. In essence, a pulse of NO and NH_3 is fed to the freshly calcined catalyst and the nitrogen resulting from the reaction

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

is monitored. The amount of N_2 formed in the initial part of the resulting pulse response is taken to represent the total number of V=O that which are probably located at exposed (010) surfaces.

Gases. $^{18}O_2$ (isotopic purity 99 atom %) was obtained from MSD Isotopes (Montreal, Canada) and was used without further purification. $^{18}O_2$ means $^{18}O^{18}O$. Mixtures of about 1000 ppm $^{18}O_2$ and $^{16}O_2$ in helium at total pressures up to 10 MPa were prepared by conventional static gravimetric methods in our laboratory. The gas mixtures of NO (2200 ppm) and of NH_3 (2000 ppm) in helium were purchased from Air Products and were used without further purification. The gas mixtures of NO, NH_3, and O_2 used in the experiments were made up of the different mixtures with the aid of mass-flow controllers (Matheson).

Apparatus. The reaction system used, which is shown in Figure 1, consists of a gas-mixing system, a reactor with oven, and a mass spectrometer; all parts were controlled and monitored by an Apple II data system. The equipment was constructed in such a way that labeled compounds could be introduced into the reactor during the selective catalytic reduction. All tubing located between the

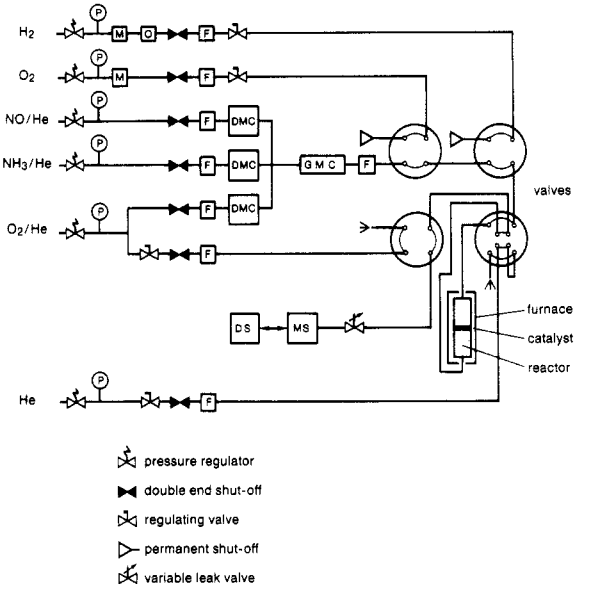

Figure 1. Apparatus used to study the reaction of NO, NH_3, and O_2. The whole system is processed by an Apple II computer. DMC, digital mass-flow controller; DS, data system; F, in-line filter (7 μm); GMC, gas-mix chamber; M, moisture trap; MS, mass spectrometer; O, oxygen trap; P, pressure gauge.

reactor and the mass spectrometer was kept at 120–140 °C in order to avoid adsorption of the various compounds on the walls of the tubing. Neither the quartz steady-state plug-flow reactor nor the stainless steel tubing showed any catalytic activity during the experiments; in addition, no exchange was observed between the labeled compounds used and the quartz up to a temperature of 400 °C. The rate of flow through the reactor (inner diameter 8 mm) was about 100 $cm^3 \cdot min^{-1}$ (STP). Isotopic and product analysis were performed with a magnetic mass spectrometer (Finnigan MAT 112) connected with the reactor outlet via an adjustable leak valve.

Procedures. The reaction was studied at 300, 350, and 400 °C over the monolayer catalyst V_2O_5 on TiO_2 (**1**) but at only 400 °C for the other catalysts. All experiments (except in the case mentioned in Figure 2) were carried out with 50 mg of catalyst, with a total flow of 100 $cm^3 \cdot min^{-1}$ (STP) of a gas mixture of 500 ppm of NO (with 21 ppm of Ar), 500 ppm of NH_3 (with 25 ppm of Ar), and about 600 ppm of O_2, the balance being helium. The Ar was used to check the stability of the mass spectrometer during the measurements.

The transients were generated by abruptly changing, for example, the composition of the feed, from a mixture containing $NO/NH_3/^{18}O_2$ to a mixture containing $NO/NH_3/^{16}O_2$ and vice versa. The time delay from the catalyst/reactor to the mass spectrometer was determined by measuring the response curves of the various compounds (relaxation curves) in the absence of a catalyst. The time-delay values for NO, N_2O, and O_2 were 30 s and for H_2O and NH_3 10 and 30–40 min, respectively. The gas mixture coming from the reactor was monitored on-line at regular time intervals (2 min) with a scanning rate of 50 mass units/s; a range of m/e = 13 up to 50 was scanned to monitor the concentrations of ammonia, nitric oxide, and oxygen and the reaction products nitrogen, nitrous oxide, water, and their isotopic isomers.[1]

The mass spectrometer was calibrated with known concentrations of the compounds before each measurement. The accuracy of each measurement of isotopic composition was determined by the material balance of N, ^{16}O, ^{18}O, and H. The mass balance of N, O, and H were obtained by comparing the quantities of N, O, and H introduced by the compounds NO, O_2, and NH_3 and the quantities of N, O, and H present in the reaction products. The material balances were found to be in agreement up to a margin of 10%, except for measurements with catalyst **1** at 350 °C, after which strong deviations were obsered for the H, ^{16}O, and ^{18}O balances. The detection limit for all compounds was about 1 ppm.

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TABLE II: Summary of Product Distribution (ppm) at Steady-State Conditions for NO-NH_3-$^{18}O_2$ (Except the Concentrations of Ammonia) on Various Catalysts[a]

catalyst no.[b]	temp, °C	NO	$^{18}O_2$	$N^{18}O$	N_2	H_2O	$H_2{}^{18}O$	N_2O	$N_2{}^{18}O$	$S_{N_2{}^{18}O}$[c]	$S_{H_2{}^{18}O}$[c]
		500	455	0	0	0	0	0	0		
1	400	65	299	28	330	397	284	66	24	0.27	0.42
1	350	82	351	17	370	579	177	20	4	0.17	0.23
1	300	103	377	16	349	356	143	3	0	0.00	0.29
		500	581	0	0	0	0	0	0		
2	400	188	520	45	245	342	111	19	4	0.17	0.15
3	400	209	527	35	258	459	100	8	1	0.11	0.18
4	400	176	514	42	238	309	70	13	1	0.47	0.18
5	400	208	504	125	153	304	229	169	81	0.32	0.32

[a] $[NO]_i = [NH_3]_i = 500$ ppm. $[^{18}O_2]_i = 455$ ppm for catalyst **1**, and for catalysts **2–5** $[^{18}O_2]_i = 581$ ppm. [b] See Table I. [c] $S_{N_2{}^{18}O} = [N_2{}^{18}O]/([N_2O] + [N_2{}^{18}O])$. $S_{H_2{}^{18}O} = [H_2{}^{18}O]/([H_2O] + [H_2{}^{18}O])$.

TABLE III: Components Formed or Components Reacted during the Non Steady State (0–280 min)[a]

		components formed			^{18}O[d]	^{18}O[e]	O[f]
catalyst no.[b]	temp, °C	$H_2{}^{18}O$[c]	$N_2{}^{18}O$[c]	$N^{18}O$[c]	converted	uptake	calcd
1	400	284	23	20	363	36	47
1	350	190	0	17	242	35	47
1	300	140	0	16	182	26	47
2	400	86	4	38	142	14	137
3	400	75	0	25	126	26	196
4	400	54	0	37	156	65	108

[a] Amount of catalyst, 50 mg. Quantities in micromoles. [b] See Table I. [c] Graphically integrated area under the curves of concentration versus time. [d] Calculated from the amount of reacted oxygen (Table V). [e] Consumed ^{18}O, which was incorporated in the catalyst during the reduction reaction of NO with NH_3. [f] Calculated oxygen content for the V_2O_5 component of the catalyst.

Results

The catalysts listed in Table I were selected because of the difference in their surface area and the differences in the types of support. Table I also gives the surface concentration of V=O groups initially present on the catalysts. These concentrations were determined by using the pulse technique at 375 °C for catalyst **1** and at 400 °C for the others. Above 350 °C the initial pulse response, which is related to the number of V=O groups (or active sites), remains constant for any catalyst;[18] the figures given in the last column of Table I can thus be compared. The value for the unsupported V_2O_5 sample is calculated from the one given in ref 17, taking into account a specific surface area of 10.5 $m^2 \cdot g^{-1}$ compared with a value of 5.4 $m^2 \cdot g^{-1}$ for the sample used there.

Figure 2 shows the concentration levels of the reactants and products as a function of time over 100 mg of the V_2O_5 on TiO_2 catalyst at a temperature of 400 °C following calcination of the catalyst at 300 °C in a flow of O_2. The concentration of a number of molecular species are plotted from the start of the reaction. The curve of H_2O deviates from the profile of a step function because of adsorption of H_2O on the tubing at the start of the reaction (see Experimental Section).

Significant features of the results are the abrupt decrease of the concentration of $^{18}O_2$, NO, and NH_3 from their initial concentrations (455, 550, and 500 ppm, respectively), the relatively slow formation of $H_2{}^{18}O$ and $N_2{}^{18}O$, and the simultaneous decrease of H_2O. The concentration of $N^{18}O$, not shown for reasons of clarity, also increases, showing the same concentration profile as that of $H_2{}^{18}O$. The concentrations of the components, except for H_2O, $H_2{}^{18}O$, N_2O, and $N_2{}^{18}O$, reach a steady state within 10 min. N_2O was only produced at temperatures above 300 °C. It is found that the area under the curve for $H_2{}^{18}O$ equals the area between the curve for H_2O and the dotted line shown at 720 ppm. The dotted line is the concentration of H_2O at steady state when O_2 is used instead of $^{18}O_2$.

Table II gives the concentrations of most of the reactants and products (except ammonia) over the catalysts under steady-state conditions for experiments such as that shown in Figure 2. In addition, the V_2O_5 on TiO_2 catalyst was measured at 300 and 350 °C. The quantity of $^{18}O_2$ consumed is seen to be largely dependent on the temperature and on the catalyst type. N_2O is always produced, irrespective of the presence of labeled oxygen. In the presence of oxygen-18, $N^{18}O$, $H_2{}^{18}O$, and $N_2{}^{18}O$ are also found.

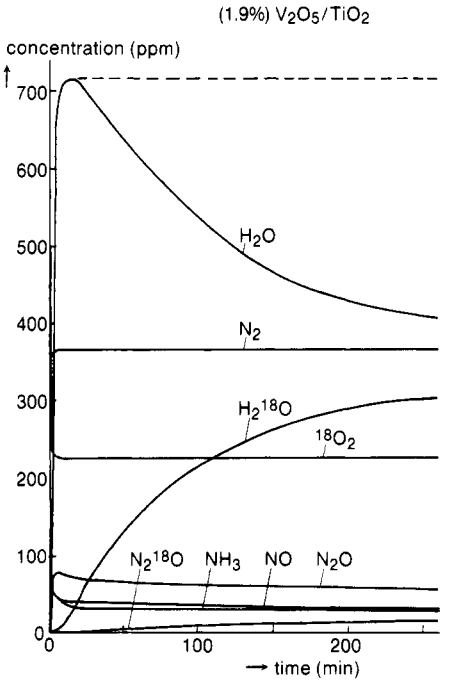

Figure 2. Concentration profiles of NO, NH_3, $^{18}O_2$, N_2O, and $N_2{}^{18}O$ over the catalyst V_2O_5 on TiO_2 (100 mg) at 400 °C after calcination in O_2 at 400 °C: $[NO]_i = [NH_3]_i = 500$ ppm; $[^{18}O_2]_i = 455$ ppm; balance helium. The concentration of $N^{18}O$ has been omitted.

We found no evidence for the formation of $O^{18}O$ as a result of exchange of bulk oxygen of supported catalysts with $^{18}O_2$ according to the reaction

$$^{18}O_2 + V{=}O \rightarrow O^{18}O + V{=}{}^{18}O$$

Hence, we conclude that this so-called scrambling[19-21] process of the gaseous or adsorbed oxygen does not occur with lattice oxygen in the temperature region of 300–400 °C. In the transient isotopic tracer experiments, oxygen of the catalyst was exchanged by labeled oxygen at 400 °C (Table III). Assuming that only the oxygen species of the vanadia part of the supported catalysts has been exchanged, it can be calculated from the figures in Table III that between 10 and 77% of the oxygen initially present in

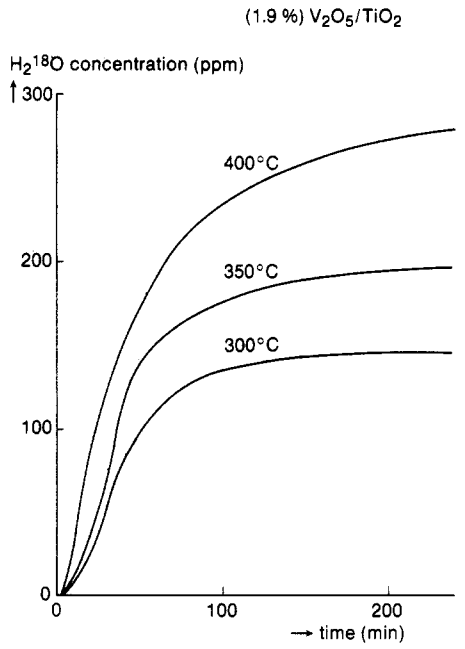

Figure 3. Concentration profiles of the reaction product $H_2{}^{18}O$ at three temperatures for the catalyst V_2O_5 on TiO_2: $[NO]_i = [NH_3]_i = 500$ ppm; $[O_2]_i = 455$ ppm; balance helium. The catalysts (50 mg), used in the separate experiments, were first calcined at 300 °C for 1 h in a gas mixture of 25% O_2 in helium (100 $cm^3 \cdot min^{-1}$ (STP)).

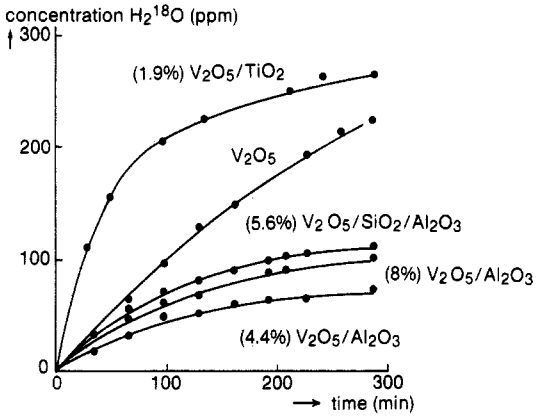

Figure 4. Concentration profiles for the various catalysts at 400 °C. $[NO]_i = [NH_3] = 500$ ppm; $[{}^{18}O_2]_i = 581$ ppm, except for the experiments with catalyst V_2O_5 on TiO_2, where $[{}^{18}O_2]_i = 455$ ppm; balance helium. The catalysts were calcined at 300 °C in a (25%) O_2/He flow for 1 h (100 $cm^3 \cdot min^{-1}$ (STP)).

the vanadia part of the catalyst can be replaced. The catalyst with the highest exchangeability of oxygen is the monolayer V_2O_5 on TiO_2 (**1**) catalyst. The column (Table III) of ^{18}O uptake was obtained by subtracting the amount of $^{18}O_2$ consumed by the reaction of NO and NH_3 with the total amount of ^{18}O present in the reaction products $H_2{}^{18}O$, $N_2{}^{18}O$, and $^{18}O_2$. It should be stressed that the values presented in Table III are the number of micromoles of components formed or adsorbed during the non steady state.

Figure 3 shows the effect of the temperature on the formation of $H_2{}^{18}O$ as a function of time in similar experiments, carried out on each occasion with a freshly calcined sample of the V_2O_5 on TiO_2 catalyst. $H_2{}^{18}O$ profiles with the other catalysts are shown in Figure 4. The catalyst with the lowest vanadia loading and the smallest specific surface area produces the most $H_2{}^{18}O$, both in the early stages of the reaction and in the steady state. The catalyst supported on titania shows the highest initial rate of production of ^{18}O-labeled water and also the highest steady-state value. The three other supported catalysts show a similar behavior at a lower level. The unsupported V_2O_5 behaves differently, rising very slowly to the steady-state level. The labeled oxygen that has

TABLE IV

catalyst no.[b]	temp, °C	TON[a]	$t_{1/2}$, min	τ, ks	τ(TON)
1	400	2.3×10^{-4}	35	3.0	0.7
1	350	1.7×10^{-4}	35	3.0	0.5
1	300	1.8×10^{-4}	35	3.0	0.5
2	400	2.8×10^{-5}	73	6.3	0.2
3	400	2.1×10^{-5}	78	6.8	0.1
4	400	1.4×10^{-5}	70	6.1	0.08

[a] TON is the turnover number, the number of molecules of $H_2{}^{18}O$ per site per second. $t_{1/2}$ is defined in the text. τ is the relaxation time, and τ(TON) is the number of molecules of $H_2{}^{18}O$ per site. The surface area of one V=O site is taken as 2×10^{-19} m^2.[25] [b] See Table I.

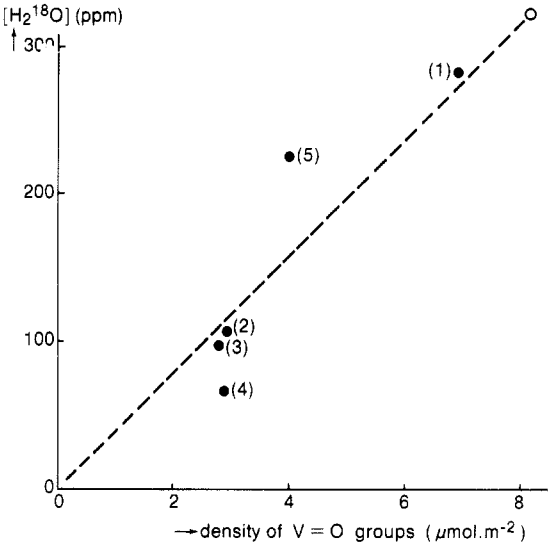

Figure 5. Relationship between the steady-state concentration of $H_2{}^{18}O$ and the density of surface V=O groups present in the catalysts. The maximum value for $\sigma_{V=O} = 2 \times 10^{-19}$ m^2. The dotted line starts at the origin and ends at the point (8.2 μmol·m^{-2}; 325 ppm $H_2{}^{18}O$). This point represents the maximum attainable $H_2{}^{18}O$ concentration when the number of the V=O surface groups is at a maximum.

reacted is mainly found in the $H_2{}^{18}O$, as can be seen from the results given in Table III. The measured curves of the concentration of $H_2{}^{18}O$ versus time shown in Figures 2, 3, and 4 can, between 15 and 110 min, be described as exponential functions (see Discussion). The curves of $H_2{}^{18}O$ do not fit the exponential relationship mentioned above in the first 15 min of the reaction. The $t_{1/2}$ values, defined as the time when half of the steady-state concentration of $H_2{}^{18}O$ has been produced in the curves of Figures 3 and 4, are given in Table IV. The values vary between 35 and 78 min. The $t_{1/2}$ time was found to be the same at each of the temperatures examined for the catalyst V_2O_5 on TiO_2 (**1**). The relaxation time τ can be obtained by calculating $t_{1/2}/\ln 2$. τ(TON) is a measure for the upper limit of the fractional coverage of OH groups (see Discussion).

The steady-state concentration of $H_2{}^{18}O$ is plotted in Figure 5 against the density of the surface V=O groups. The density is calculated by means of the ratio of the number of surface V=O groups (determined by pulse experiments) and the total surface area (BET). A roughly linear relationship exists. (It should be noted that there is no direct proportionality between the rate of exchange to give $H_2{}^{18}O$ and the total number of V=O groups.) It was also observed that three groups of catalysts can be distinguished: the alumina-based catalyst, the titania-based catalyst, and pure vanadia. Both the selectivity to $N_2{}^{18}O$ [defined as $[N_2{}^{18}O]/([N_2{}^{18}O] + [N_2O])$] and to $H_2{}^{18}O$ increases with the surface density of V=O groups (Table II). When the isotopic composition of oxygen in the feed was changed, the concentration of $N_2{}^{18}O$ and of $H_2{}^{18}O$ were found to drop very rapidly, as is shown in Figure 6. The form of these curves is also exponential.

The quantities of $H_2{}^{18}O$ (in micromoles) formed at non steady state at 400 °C were calculated for the first 280 min by means of graphical integration of the curves of Figures 3 and 4, and the

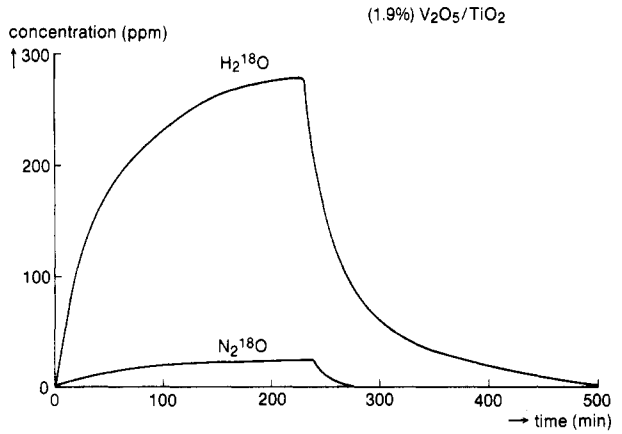

Figure 6. Transient profile of $H_2{}^{18}O$ during the reaction of NO, NH_3, and oxygen. After 230 min the isotopic composition was abruptly changed from $^{18}O_2$ to $^{16}O_2$.

TABLE V: Apparent Reaction Rates (Atoms of Oxygen·m^{-2}·h^{-1}) as a Function of Temperature of the Reaction of NO, NH_3, and Oxygen on the Catalyst V_2O_5 on TiO_2 (1) at Different Temperatures and at 400 °C on Catalysts 2–5

catalyst no.[a]	temp, °C	O_2,[b] ppm	r	r,[c] V_2O_5
1	400	158	2.1×10^{19}	4.8×10^{19}
1	350	103	1.4×10^{19}	1.8×10^{19}
1	300	77	1.0×10^{19}	0.6×10^{19}
2	400	61	0.8×10^{19}	
3	400	53	0.7×10^{19}	
4	400	67	0.9×10^{19}	
5	400	77	1.0×10^{19}	

[a] See Table I. [b] O_2 consumption in the steady state. [c] Calculated from data of ref 29.

results are given in Table III. It turns out that the consumption of oxygen-18 by the catalyst surface at 400 °C varies between 10 and 77% of the oxygen present in the vanadia of the catalyst (Table III) and that although this amount is dependent on the reaction temperature, it is always less than the calculated quantity of oxygen in the V_2O_5 of the catalyst.

From the oxygen-18 consumed by the catalyst and the specific surface area, an apparent reaction rate, defined as the number of atoms of oxygen reacting in the steady state per unit-specific surface area per hour, can be calculated (Table V). The apparent rates of reaction of oxygen-18 for the catalyst V_2O_5 on TiO_2 (1) are comparable with those of vanadia. Hence the behavior of V_2O_5 on TiO_2 (1) and unsupported V_2O_5 are about the same with respect to the consumption of oxygen.

In order to find the answer to the question whether ^{18}O remains present in the catalyst or not, ^{18}O was introduced into the catalyst at 400 °C. This resulted in a labeled catalyst. This was done by pretreating the monolayer catalyst first with a gas mixture of NO, NH_3, and $^{18}O_2$ at 400 °C. The catalyst was then kept in helium at 400 °C for 15 h. According to Table III the monolayer catalyst had adsorbed 36 μmol of ^{18}O at 400 °C. This value corresponds to the difference between the total amount of ^{18}O that was consumed by the reaction and the total amount of ^{18}O present in the products $H_2{}^{18}O$, $N_2{}^{18}O$, and $N^{18}O$. Figure 7 shows the result of a reaction of NO, NH_3, and O_2 over the labeled V_2O_5 on TiO_2 catalyst. The integrated area of the peak of Figure 7 corresponds to 17.5 μmol of ^{18}O. Hence, 18.5 μmol of ^{18}O of that had been added to the surface during the NO/NH_3/$^{18}O_2$ reaction and was then removed after the catalyst was flushed with helium at 400 °C overnight, before the reaction with the mixture containing O_2 was carried out.

Discussion

Role of Oxygen at the Surface of the Catalyst. The extended mechanism is shown in Figure 8. Reaction 4 has already been discussed in the literature, and it was shown by Miyamoto et al.[17] that the V=O species of supported vanadia catalysts plays an

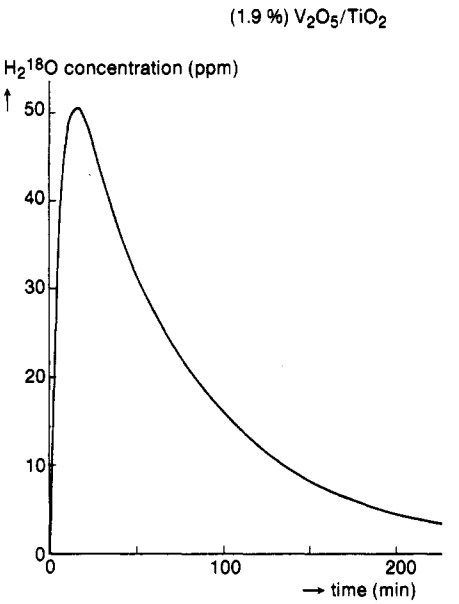

Figure 7. Concentration profile of $H_2{}^{18}O$ when the feed is changed from NO, NH_3, and $^{18}O_2$ to helium at 400 °C for 15 h and then changed abruptly to NO, NH_3, and $^{16}O_2$.

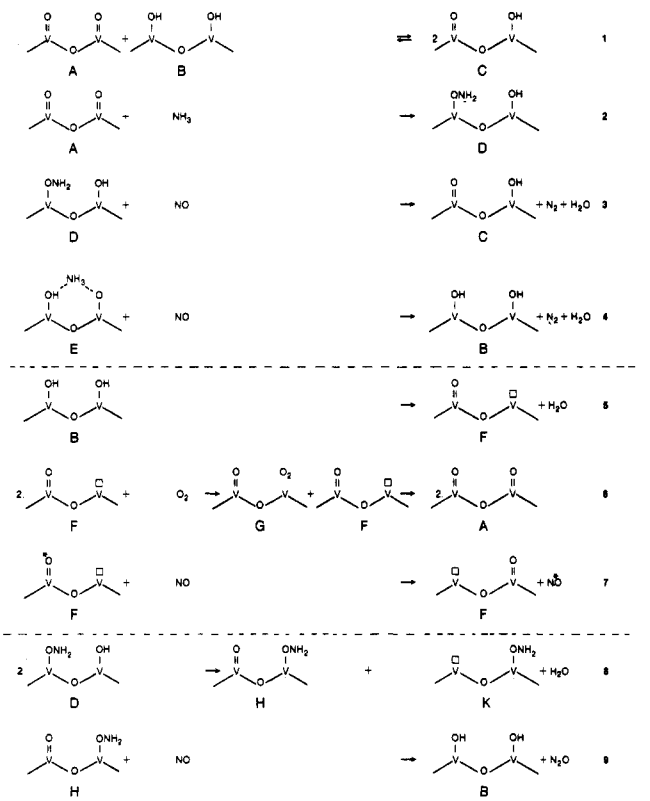

Figure 8. Mechanism for the reaction of NO, NH_3, and O_2 on a supported vanadia catalyst and formation of N_2 and H_2O via an Eley-Rideal reaction.

important role in the selective catalytic reduction of NO with ammonia both in the presence and in the absence of gaseous oxygen (step 4 in Figure 8). The rate of the reaction is markedly enhanced by gas-phase oxygen.[1-4] V=O was identified by various techniques as the active surface site.[3,5,17] In the proposed mechanism,[17] V=O is reduced to V—OH, which is then reoxidized by gaseous oxygen or oxygen from the underlying layers. However, only indirect evidence has been given for the existence of V–OH groups during the reaction, and the role of oxygen as an accelerator of the reduction of NO by NH_3 has still not been established. A modified mechanism was put forward in a previous paper,[14] in which it was concluded that oxygen from the underlying layers in monolayer catalysts does not play an important role in

the overall reaction. In the following discussion a modified and extended reaction mechanism is proposed in which light is thrown on the role of oxygen.

At the start of the reaction, and probably also during its course, three combinations of the groups V=O and V—OH, A, B, and C, can be thought of as being present on the surface of the catalyst. Due to the mobility of the protons of the OH groups, these species are in equilibrium according to reaction 1 (Figure 8). Species B can be considered as the hydrogenated form of species A and C. We assume that the number of species A in an oxygen-rich atmosphere is greater than that of species B and C. Ammonia is assumed to adsorb differently on species A and C. (i) It may be dissociatively adsorbed on species A according to reaction 2 (Figure 8), a step that involves breaking of the N—H bond in ammonia; two V=O groups are reduced by one ammonia molecule to form species D. This complex D may react with NO via an Eley-Rideal mechanism, reforming species C as shown reaction 3 of Figure 8. (ii) Alternatively, ammonia may adsorb physically on species C a Brønsted site,[3,5,19-21] and the species E formed can then again react with NO according to an Eley-Rideal mechanism (reaction 4). This step also appears in the mechanism proposed by Miyamoto et al.[5] Both the chemisorbed ammonia species D and the physisorbed ammonia species E are thus able to react with nitric oxide via an Eley-Rideal mechanism, resulting in the formation of species C and B, respectively, water and nitrogen being formed in both cases. Water formed in this way would contain oxygen from the nitric oxide, assuming that the V–O bonds at the surface remain intact.

The next step in the mechanism, reaction 5, is dehydration of the surface, creating an oxygen vacancy (V□). Here oxygen from the surface is used. Thus, during the allover reaction of the catalytic reduction of NO, two types of water are formed: that originating from the reaction of gaseous NO with adsorbed NH_3 (reactions 3 and 4) and that formed as a result of the dehydration of OH groups present on the surface of the catalyst (reaction 5). The latter reaction is relatively slow compared with the former, which can be concluded from the shape of the curves of $H_2{}^{18}O$ in Figures 2 and 3 in the first 15 min of the reaction. Evidence for the dehydration is obtained when $^{18}O_2$ is used instead of $^{16}O_2$. As can be seen in Figure 2, the oxygen concentration drops immediately and remains constant during the course of the reaction; however, the rate of formation of $H_2{}^{18}O$ is relatively slow compared with the rate of decrease of $^{18}O_2$. A possible explanation for this behavior is that the molecular oxygen initially adsorbed during the reaction does so on a single site, as shown in reaction 6 of Figure 8. When a vacancy arises next to the adsorbed oxygen molecule, the molecule dissociates and one of the atoms becomes adsorbed on the vacancy, with the other remaining on the original site. Oxygen can thus enter into the catalyst surface in a single step. This phenomenon was already observed by Hirota et al.[22] in the case of the oxidation of carbon monoxide over a V_2O_5 catalyst; the role of gaseous oxygen here was to replenish the lattice oxygen consumed by the reaction with CO.

At the beginning of the reaction, the necessary pairs or clusters of vacancies are provided by the equilibrium oxygen-deficient state of the oxide and the oxygen vacancies created by the reduction of NO with NH_3. Supported V_2O_5 and unsupported V_2O_5 catalysts contain many defects (oxygen vacancies) on the surface. As the reaction in the presence of oxygen continues, there are few vacancies left on the surface because every vacancy is immediately occupied by one oxygen molecule. The rate-determining step in the reaction is thus the dehydration of the surface, and the oxygen of the surface is involved in the formation of water.

One of the types of surface groups present during the course of the reaction is V–OH, and the question still remaining is what the number of these groups on the working catalyst is. The relaxation curves shown in Figures 3 and 4 can be used to calculate an upper limit for this number according to the procedures described by Biloen et al.;[23] the results are given in Table IV. Biloen and co-workers have used such transient behavior in experiments on methanation and Fisher–Tropsch catalysis[23,24] in order to obtain transient kinetic information without disturbing the steady-state situation. They showed that the response (or relaxation) time τ, the coverage in surface intermediates θ_i (defined as the ratio of the number of surface intermediates and the number of surface-exposed catalyst atoms), and the turnover number, under certain restrictions, are related:

$$\mathrm{TON} = \theta_i \tau$$

This relationship will now be discussed briefly. Suppose that an arbitrary area of the catalyst surface, containing N_s surface oxygen atoms, is covered with a pool of N_i OH groups (the sum of the number of ^{18}OH and ^{16}OH groups) and produces R $H_2{}^{18}O$ molecules per second under steady-state conditions. The relation between time and the pool's isotopic composition, which is related to the ratio of the number of ^{18}OH groups and the total number of OH groups present on the surface, can be then described by

$$F(t) = 1 - e^{-t/\tau}$$

where t is the time and

$$\tau = N_i/R = t_{1/2}/\ln 2$$

N_i/R can also be written as $(N_i/N_s)/(R/N) = \theta_i/\mathrm{TON}$. The relaxation curves, shown in Figures 3 and 4, are almost purely exponential between 15 and 110 min and may be characterized by an exponential equation of the form

$$F(t) = 1 - e^{-t/\tau}$$

where $F(t) = [H_2{}^{18}O]/[H_2{}^{18}O]_\infty$, $[H_2{}^{18}O]_\infty$ being the concentration of $H_2{}^{18}O$ in the steady state and inversely proportional to the reciprocal pseudo-first-order rate constant. The τ values can thus be converted into the θ_i values, given in Table IV. The $t_{1/2}$ values are constant at different temperatures. At 400 °C the maximum coverage of the surface with OH groups is about 0.7 for the catalyst V_2O_5 on TiO_2 (**1**) (Table IV) and has the value of 0.5 at 350 and 300 °C. This maximum coverage decreases as the specific surface area increases and as the number of active sites, represented by the number of V=O groups per gram of catalyst, increases.

The activities of the V_2O_5 on TiO_2 and V_2O_5 on SiO_2/Al_2O_3 catalysts and the V_2O_5 on Al_2O_3 and the unsupported V_2O_5 catalysts are 80–90% and 58–65%, respectively, suggesting that the number of active sites is almost the same for each of the two groups of catalysts. Thus, at constant activity, both the selectivity of $H_2{}^{18}O$ to H_2O and the maximum coverage of the surface with OH groups decrease (Table II). However, the ^{18}O consumption of the surface increases with increasing specific surface area and vanadium content of the catalysts. This leads to two conclusions: (i) the surface is covered with OH groups which are distributed randomly; and (ii) the number of adjacent OH groups decreases with increasing surface area. For the formation of gaseous water from two OH groups on the surface (reaction 5 of Figure 8), it is necessary that these OH groups are adjacent. As the reaction proceeds, two or more adjacent OH groups are produced when ammonia reacts with gaseous nitric oxide (reaction 4). This dual-site mechanism is illustrated by the results of Figure 5, where the concentration of $H_2{}^{18}O$ formed in the steady state is plotted as a function of the "density" of the V=O groups. This relationship demonstrates the statistical character of the process: the higher the density of V=O groups, the higher the number of adjacent sites. From the number of V=O groups on the surface

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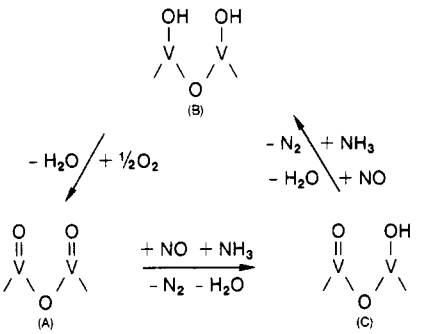

Figure 9. Summarized reaction mechanism of the selective catalytic reduction of NO with NH_3 in the presence of oxygen.

and the specific surface area, the surface density was calculated. The rate of $H_2{}^{18}O$ exchange is thus related to the density of surface V=O groups. In a similar way the turnover numbers calculated from the dynamic exchange experiments are also related to the density of V=O species shown in Figure 3.

The plot in Figure 5 may reflect the specific exposure of (010) crystal planes as the only planes containing V=O groups. It was shown by Miyamoto et al.[17] that about 50% of the surface area of unsupported V_2O_5 consists of (010) planes. It is significant that the maximum density of V=O species which could be accommodated on the vanadium–titanium monolayer material, assuming that the whole surface is covered by V=O groups, is 8.2 μmol·m^{-2}; 80% of this is achieved (see Figure 5). This is probably due to the perfect fit of the (010) planes of V_2O_5 to the planes of anatase, as has been shown by Vejux and Courtine.[26] It is recognized[25,27] that such a monolayer does not possess the structure of pure V_2O_5. In contrast to the results for the titania-supported materials, alumina and alumina/silica carriers do not offer such an epitaxial fit, and the supported V_2O_5 exposes fewer (010) planes, and hence fewer active sites, than unsupported V_2O_5.

In Figure 9 a reaction mechanism is proposed; this involves a series of steps giving rise to reduction and reoxidation of the surface. Each of the steps represents a combination of the reactions shown in the scheme of Figure 8.

Role of Oxygen in the Catalyst. It is assumed that integration of the curve between 230 and 500 min in Figure 6 represents the maximum amount (about 47 μmol; see Table III) of the exchangeable oxygen present in the catalyst. However, when the feed was not instantly changed but the catalyst was first flushed in helium for 15 h, half of the amount of ^{18}O previously adsorbed by the catalyst had disappeared or was not available for reaction with the NO and NH_3 mixture. We suggest that the oxygen-18 had diffused into the support of the catalyst via oxygen vacancies and that oxygen-16 had diffused in the opposite direction. This process is relatively slow. The exchange experiments in general showed that ^{18}O is readily incorporated into the reaction product water and that ^{18}O, present on the surface, can easily be replaced by ^{16}O. The presence of exchangeable oxygen in vanadium pentoxide, particularly the oxygen of the V=O groups, has previously been shown by using an infrared technique.[28] WO_3, MoO_3, and V_2O_5 have been reported to exchange the whole of their lattice oxygen with the gas phase, the diffusion of oxygen through the solid being faster than the surface exchange, which is therefore rate determining.[29-31] Rates of about 10^{18} atoms·m^{-2}·h^{-1} at temperatures in the range of 553–747 °C have been mentioned in the literature.[31] This extraordinarily high reactivity and lability of the bulk oxygen of the oxides is explained in terms of structural defects in the bulk:[31] distorted octahedra connected with each other along common edges or corners. $N^{18}O$ is formed during the reaction, and we therefore conclude that NO is dissociatively adsorbed on the surface in such a way that the oxygen species can be exchanged according to reaction 7 (Figure 8). A study about the formation of $N^{18}O$ will be presented in a forthcoming paper.

Formation of N_2O. The reaction mechanism presented above is not complete. One of the questions left is how and on what type of site N_2 and N_2O are formed. From the literature, it is well-known that both this N_2 and this N_2O are produced from one nitrogen atom of the NH_3 and that from the NO,[5,7,8] but the nature of the site or sites on which these reactions take place is not known. The formation of N_2O can be explained by reaction 9 in Figure 8. NO reacts with species H, and at the same time two V=O groups are reduced to V—OH groups; species H can be formed through a reaction such as step 8 (Figure 8).

Another possibility is that a vacancy of the type associated with species F can be reoxidized with gaseous oxygen or with nitric oxide. In the reoxidation by NO, this molecule adsorbs on an oxygen vacancy. If two vacancies are formed side by side, N_2O can be produced directly, leaving one oxygen atom on the vacancy, and species F is regenerated. In a forthcoming paper we will discuss the role of ammonia in the mechanism and the cause of nitrous oxide formation during the reaction of NO and NH_3.[32]

Conclusions

Oxygen atoms from both lattice and NO participate in the formation of water and nitrous oxide. A more detailed mechanism based on the experimental results with nitrogen and oxygen tracers has been proposed for the reaction of NO with NH_3 in the presence of oxygen. All the phenomena observed could be explained in terms of the proposed mechanism. Oxygen atoms of vanadia participate in the reaction of nitric oxide and ammonia and are exchanged during the reaction with gaseous oxygen. We have been able to establish that the process involving displacement of oxygen from the surface is not accompanied by isotopic scrambling, which suggests that O_2 is adsorbed by the catalyst as molecular oxygen. The formation of $N^{18}O$ can be explained by assuming scrambling of NO with V=^{18}O groups.

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Registry No. NO, 10102-43-9; NH_3, 7664-41-7; O_2, 7782-44-7; V_2O_5, 1314-62-1; TiO_2, 13463-67-7.

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